

AD-A200 301

DTIC FILE COPY

2

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470-P00003

R&T Code NR 33359-718

Technical Report No. 93

An in situ Infrared Study of the Oxidation of SO_2 on Platinum Electrodes

by

C. Korzeniewski, W. McKenna and S. Pons

Prepared for publication in J. Electroanal. Chem.

Department of Chemistry
University of Utah
Salt Lake City, UT 84112

July 15, 1988

DTIC
ELECTE
NOV 14 1988
S D
H

Reproduction in whole, or in part, is permitted for
any purpose of the United States Government

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

88 11 11 11

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 93			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of Utah		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Henry Eyring Building Salt Lake City, UT 84112			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0470-P00003		
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program, Code 1113 800 N. Quincy Street Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) An <u>in situ</u> Infrared Study of the Oxidation of SO ₂ on Platinum Electrodes					
12. PERSONAL AUTHOR(S) C. Korzeniewski, W. McKenna and S. Pons					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 9/87 TO 7/88		14. DATE OF REPORT (Year, Month, Day) July 15, 1988	
15. PAGE COUNT 24					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) infrared spectroelectrochemistry, sulfur dioxide		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Attached.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> NOT DESK			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Stanley Pons			22b. TELEPHONE (Include Area Code) (801)581-4760		22c. OFFICE SYMBOL

AN IN SITU INFRARED STUDY OF THE OXIDATION OF
SULFUR DIOXIDE ON PLATINUM ELECTRODES

by

Carol Korzeniewski*, William McKenna**, and Stanley Pons

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

*Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109.

**Eastman Kodak Co., Kodak Research Laboratory, B-204, Building 82
Rochester, NY 14650.

The oxidation of sulfur dioxide on metal electrodes is of interest for its application in a variety of industrial processes, particularly in operations involving degradation of automobile emissions, production of energy, and winning of sulfide ores. The oxidation of sulfur dioxide by electrochemical methods is a complex process in which intermediates and products are formed which strongly adsorb on the electrode surface. A large number of electrochemical investigations have appeared which employ voltammetric techniques to obtain mechanistic information about the process (1-6). However, the oxidation process at platinum electrodes is a strong function of electrode pretreatment at cathodic potentials; thus, the electrochemical studies are not all in agreement. *Electrochem. Soc.*

Studies using cyclic voltammetry indicate that when SO_2 is introduced into an aqueous acid solution held at potentials about +0.25 V (SCE) (near the open circuit potential) oxidation of SO_2 begins at about +0.5 V (SCE) and is rapidly poisoned by formation of surface oxide species at more anodic potentials (3,5,6). Separate mechanisms have been proposed for the oxidation on clean and oxide covered platinum surfaces at these potentials. When the potential is swept cathodic following the initial oxidation sweep, an anodic peak appears at about 0.6 V (SCE) (5,6). At potentials in the hydrogen evolution region two cathodic waves appear which have been assigned to reduction of SO_2 to form adsorbed sulfur species which alter the electrochemistry of subsequent oxidation cycles. The nature of this surface species and the effect on the oxidation process have been the target of several electrochemical investigations (3,6).

In this analysis, an in situ infrared spectroscopic study of the oxidation of sulfur dioxide on platinum electrodes is undertaken. The focus of this investigation is on the oxidation processes which occur at potentials in the double layer region and where platinum oxide is formed. Also presented are spectra collected at cathodic potentials, where the surface activating sulfur



A-1

Spec 1

species is believed to form.

The experiments were performed in a three electrode cell made from a glass syringe (JAS Instrument Systems) (7). A CaF_2 infrared transparent window was mounted on the front of the cell and the electrode-window distance was made as small as possible (about $1\ \mu\text{m}$). The working electrode was constructed from a disk of platinum (about 9 mm dia.) which was sealed in glass and polished to a mirror finish with alumina in decreasing particle sizes down to $0.05\ \mu\text{m}$. The electrode was cleaned by continuous cycling between $-0.25\ \text{V}$ and $+1.2\ \text{V}$ (SCE) until sharp hydrogen waves were obtained. Following cycling, the electrode potential was held at $+0.3\ \text{V}$ (SCE) and sulfur dioxide was released into the cell. All reported potentials are with reference to the saturated calomel electrode.

Infrared spectra were obtained using the method of subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) (7). As the electrode processes are irreversible, a staircase potential step scheme was used to prevent elimination of spectral information by signal averaging (8). All spectra are computed from the average of 512 interferograms and normalized to a reference spectrum obtained at $+0.3\ \text{V}$. Positive going bands are due to species present at $+0.3\ \text{V}$ and negative going bands arise from species formed at the new potential. Infrared spectra were obtained using an IBM IR/98 Series infrared spectrometer.

Solutions were prepared from analytical grade sulfuric acid (J. T. Baker) and triply distilled water. Sulfur dioxide (99.98 % Matheson) was used without further purification. The electrochemistry was controlled using a potentiostat and waveform generator (Hi-Tek Instruments).

The cyclic voltammetry of SO_2 in $1.0\ \text{M}\ \text{H}_2\text{SO}_4$ is shown in Figure 1. According to the voltammetry, on the first anodic sweep from $+0.3\ \text{V}$, SO_2 oxidation begins at about $+0.5\ \text{V}$ and is poisoned at more anodic potentials

corresponding to the onset of platinum oxide formation. On the cathodic sweep, an anodic peak is observed which has been assigned to continuing oxidation of SO_2 in the presence of the platinum oxide (6). At potentials more negative than +0.3 V two reduction peaks are observed in the voltammetry. The cathodic waves have been assigned to reduction of SO_2 to form a surface activating sulfur species. On the second sweep, both SO_2 oxidation and platinum oxide formation are diminished, behavior most likely due to an adsorbed species formed at the negative potentials.

The SNIFTIRS spectrum for the oxidation of SO_2 on clean (in the absence of platinum oxide) platinum is shown in Figure 2. The strong band appearing at 1332 cm^{-1} and the weaker band at 1151 cm^{-1} correspond to SO_2 in solution (9). The band appearing at 1168 cm^{-1} is formed as a product of SO_2 oxidation at these potentials. The spectral region between 1400 and 2000 cm^{-1} is shown in Figure 3. The sharp structure appearing in the figure is due to absorption of atmospheric water vapor. The broad band appearing at about 1650 cm^{-1} is due to loss of liquid water at the more anodic potential. The broad band at 1800 cm^{-1} arises from a product of the oxidation.

Figure 4 shows the SNIFTIRS spectrum of SO_2 oxidation at potentials where platinum oxide formation occurs. The 1332 cm^{-1} band is still apparent and formation of the 1168 cm^{-1} species still occurs. However, a shoulder at 1321 cm^{-1} now appears in the spectrum and a new band is present at 1271 cm^{-1} . The shoulder corresponds to surface SO_2 that is bonded to the platinum surface through one oxygen atom, and the 1271 cm^{-1} band occurs at energies appropriate for S-bonded SO_2 (9). Also apparent in the spectrum is a broad shift in baseline at about 1200 cm^{-1} . The position and shape of the band is characteristic of surface bound sulfate (10). Inspection of the higher energy region of the spectrum (not shown) reveals loss of water and the broad band at

1800 cm^{-1} is apparent. A visible white film forms on the electrode surface when the electrode is held at this potential for long (> 10 min) periods of time.

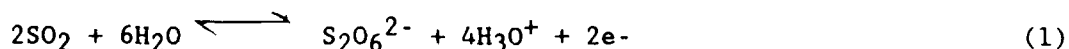
Following collection of spectra at anodic potentials, the electrode potential was returned to +0.3 V and a new set of reference spectra was collected. The potential was then stepped, according to the staircase method, to reductive potentials. The spectra collected at -0.1 V and -0.15 V are shown in Figure 5. The striking feature is loss of the 1168 cm^{-1} species to regenerate solution SO_2 as evidenced by formation of the 1332 cm^{-1} band. Also, broad bands at 1085 cm^{-1} and 989 cm^{-1} appear which correspond to formation of solution sulfate (9). Figure 6 shows a higher energy region of the spectrum. Broad bands appear at 2127 cm^{-1} , 1650 cm^{-1} , and 1800 cm^{-1} . The 1650 cm^{-1} band is due to formation of liquid water and the 1800 cm^{-1} band indicates loss of the oxidation product at these cathodic potentials. The 2127 cm^{-1} band is probably attributable to formation of a reduced sulfur species, possibly the species responsible for surface activation at cathodic potentials (3,6).

By analysis of the infrared spectra it appears that SO_2 is the electroactive species when the oxidation is carried out in aqueous acid solution. Further, it is apparent that two separate mechanisms operate for oxidation at potentials in the double layer region and at more anodic potentials where platinum oxide formation occurs. The bands pointing upward at 1332 cm^{-1} and 1151 cm^{-1} in Figures 2 and 4 arise from oxidation of solution SO_2 at +0.5 V and +0.9 V. In the absence of platinum oxide, it appears that solution SO_2 is oxidized to form a species characterized by absorption bands at 1168 cm^{-1} and 1800 cm^{-1} . When the oxidation is carried out at potentials where oxide is present on the platinum surface (+0.9 V), the spectra indicate displacement of adsorbed SO_2 , possibly by reaction with platinum oxide. A likely product of the reaction is adsorbed sulfate, as evidenced by the broad shift in base line at about 1200 cm^{-1} . A band

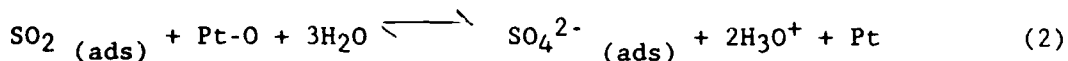
of this type is characteristic of sulfate adsorbed on a platinum electrode (10). It is unlikely that the increase in surface sulfate concentration is due to migration of sulfate from solution, as the sulfate concentration is low in solutions of sulfuric acid. The reaction of solution SO_2 also occurs at these potentials, as the 1168 cm^{-1} and 1800 cm^{-1} bands have grown, and oxidation of solution SO_2 is evident.

The oxidation of SO_2 in aqueous acid solutions gives rise to a product characterized by absorption bands at 1168 cm^{-1} and 1800 cm^{-1} . Further, reduction of this species forms solution SO_2 and water. The exact nature of this species is in question; however, electrochemical studies have suggested dithionate as a possible oxidation product (4,5). Infrared spectra obtained from Nujol mulls of sodium dithionate show absorption bands between 2300 cm^{-1} and 2000 cm^{-1} , and another strong absorption at about 1240 cm^{-1} (11). Adsorption of the dithionate species on the platinum surface could account for the strong red shifting of the infrared bands. Reduction of the species to form SO_2 and water lends further support that an adsorbed dithionate species may be involved (see Eq. 3 below); however, the exact assignment of these bands is inconclusive at the present time and further studies are underway. Reactions of adsorbed SO_2 and oxygen at platinum surfaces have been studied under vacuum conditions (12-13). The authors report formation of a sulfur-oxygen containing compound which decomposes to SO_2 and oxygen when heated; however, no identification of the product was proposed.

Assuming that adsorbed dithionate is indeed a product of SO_2 oxidation, the following mechanism is proposed from the infrared spectra:

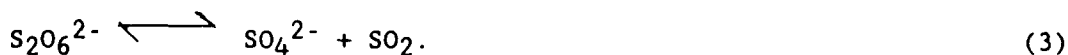


when the reaction occurs on clean platinum at potentials in the double layer region and



when the reaction occurs in the presence of platinum oxide. Studies suggest that SO_2 oxidation occurs through an SO_3^{2-} intermediate (6). However, this species was not observed in the infrared spectra, as evidenced by the absence of bands at 1010 cm^{-1} and 961 cm^{-1} in Figures 2 and 4 (9); nevertheless, this intermediate may be too short lived to detect under these conditions.

The spectra obtained when the electrode is held at cathodic potentials indicate that reaction of the 1168 cm^{-1} species occurs to form solution sulfate as indicated by broad bands at 1085 cm^{-1} and 989 cm^{-1} (9), and regenerate solution SO_2 and water. A possible mechanism for the decomposition of dithionate is given by



which would explain the increased concentration of solution SO_2 and appearance of solution sulfate.

In the cathodic limit a new species is formed which absorbs at 2127 cm^{-1} and is likely due to formation of an adsorbed sulfur species. Reduction of SO_2 may compete with the dithionate reaction at these potentials. This may explain the appearance of the 2127 cm^{-1} band; however, a positive assignment of this band can not be made with these limited spectral data.

In conclusion, a SNIFTIRS study of the oxidation of SO_2 on platinum electrodes confirms electrochemical studies which suggest that separate mechanisms operate when oxidation occurs on clean and oxide covered platinum surfaces. Infrared spectra of a major product of the oxidation are presented and the assignment of these bands to adsorbed dithionate is proposed. Further, the reduction of this product forms solution SO_2 and water, a process not previously observed using electrochemical methods.

Acknowledgments

We thank the Office of Navel Research for support of this work.

References

1. E. T. Seo, D. T. Sawyer, J. Electroanal. Chem. 7 (1964) 184.
2. E. T. Seo, D. T. Sawyer, Electrochimica Acta 10 (1965) 239.
3. A. Q. Contractor, H. Lal, J. Electroanal. Chem. 93 (1978) 99.
4. A. J. Appleby, B. Pichon, J. Electroanal. Chem. 95 (1979) 59.
5. C. Audry, M. Voinov, Electrochimica Acta 25 (1980) 299.
6. R. M. Spotnitz, J. A. Colucci, S. H. Langer, Electrochimica Acta, 28 (1983) 1053.
7. C. Korzeniewski, S. Pons, Prog. Analyt. Spectrosc. 10 (1987) 1.
8. S. Pons, M. Datta, J. F. McAleer, A. S. Hinman, J. Electroanal. Chem. 160 (1984) 369.
9. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley & Sons: New York, 1978.
10. M. W. Severson, J. Phys. Chem. (in press).
11. W. G. Palmer, J. Chem. Soc. (1962) 1552.
12. S. Astegger, E. Bechtold, Surf. Sci. 122 (1982) 491.
13. U. Koehler, H. W. Wassmuth, Surf. Sci. 117 (1982) 668.

Figure Legends

Figure 1. Cyclic voltammetry of 1.0 M H_2SO_4 (solid line) and SO_2 in 1.0 M H_2SO_4 (dashed line) at a platinum electrode. The dash-dot line is the second voltammetric sweep in the solution containing SO_2 . The current scale for the solution containing H_2SO_4 only is expanded by a factor of 10. All potentials are with reference to SCE.

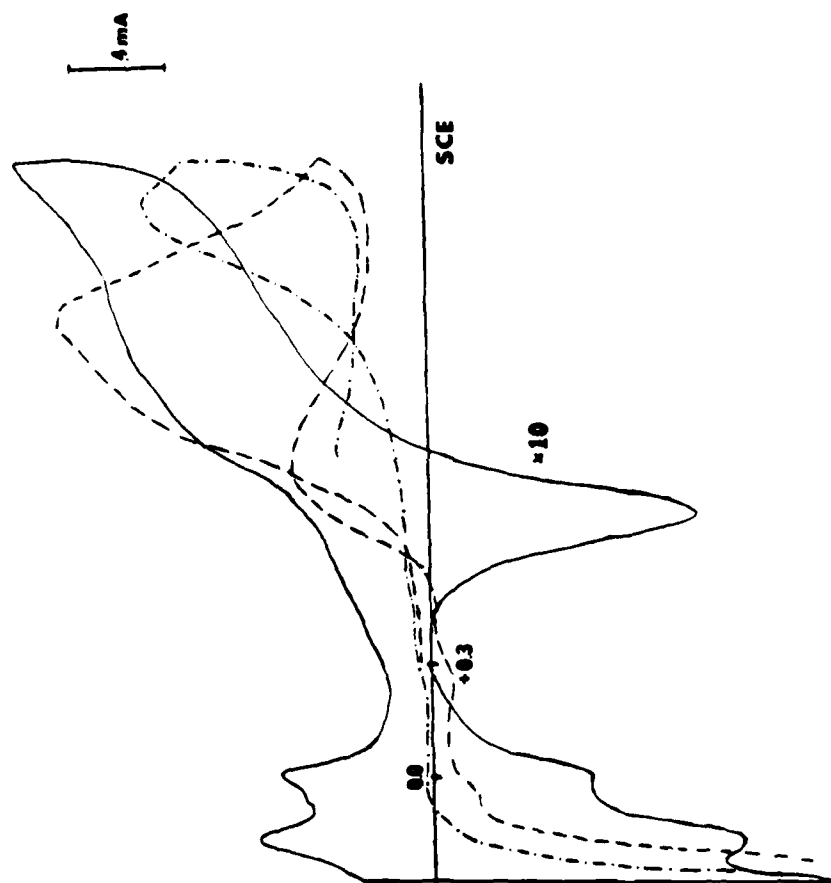
Figure 2. SNIFTIRS spectra of the oxidation of SO_2 at a platinum electrode at +0.5 V and normalized to a base potential of +0.3 V (SCE). Bands pointing upward correspond to species present at the base potential.

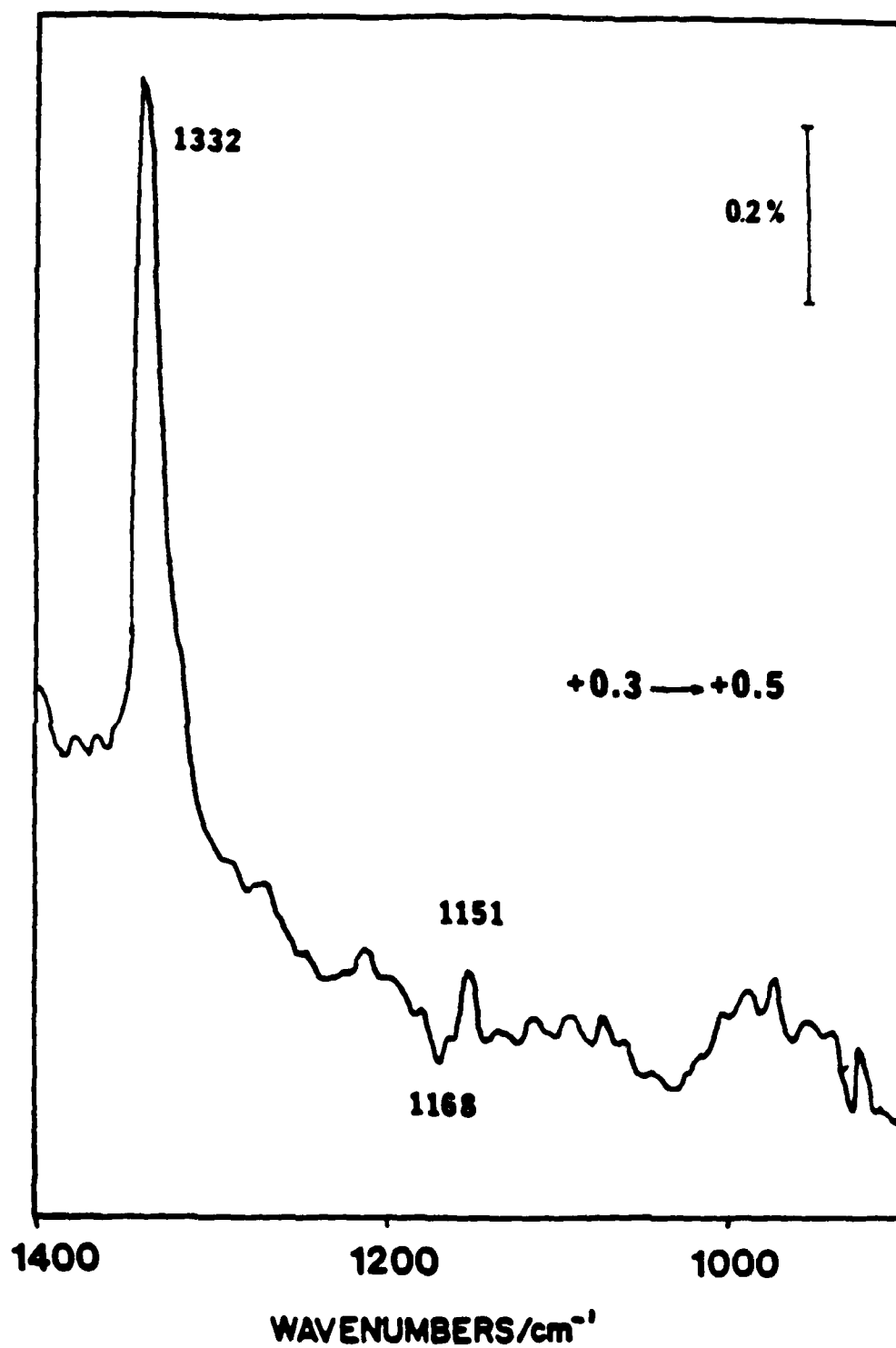
Figure 3. Same as Figure 2 showing a higher energy spectral region.

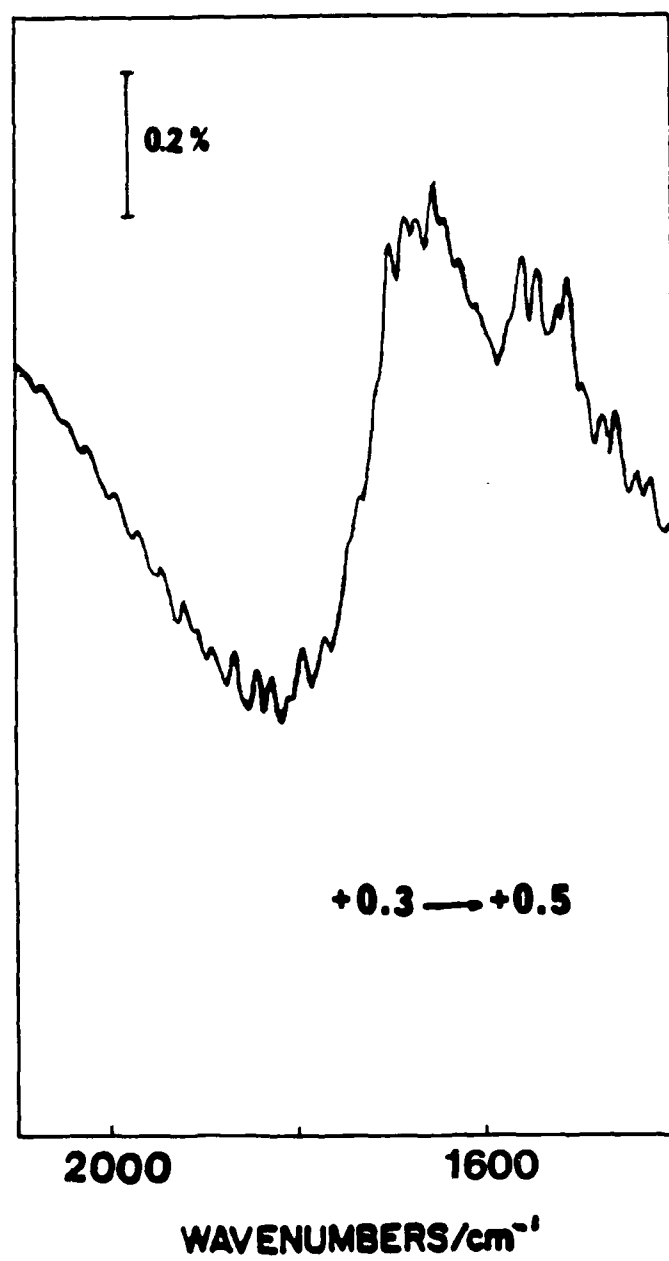
Figure 4. SNIFTIRS spectra of the oxidation of SO_2 at a platinum electrode at +0.9 V and normalized to a base potential of +0.3 V (SCE). Bands pointing upward correspond to species present at the base potential.

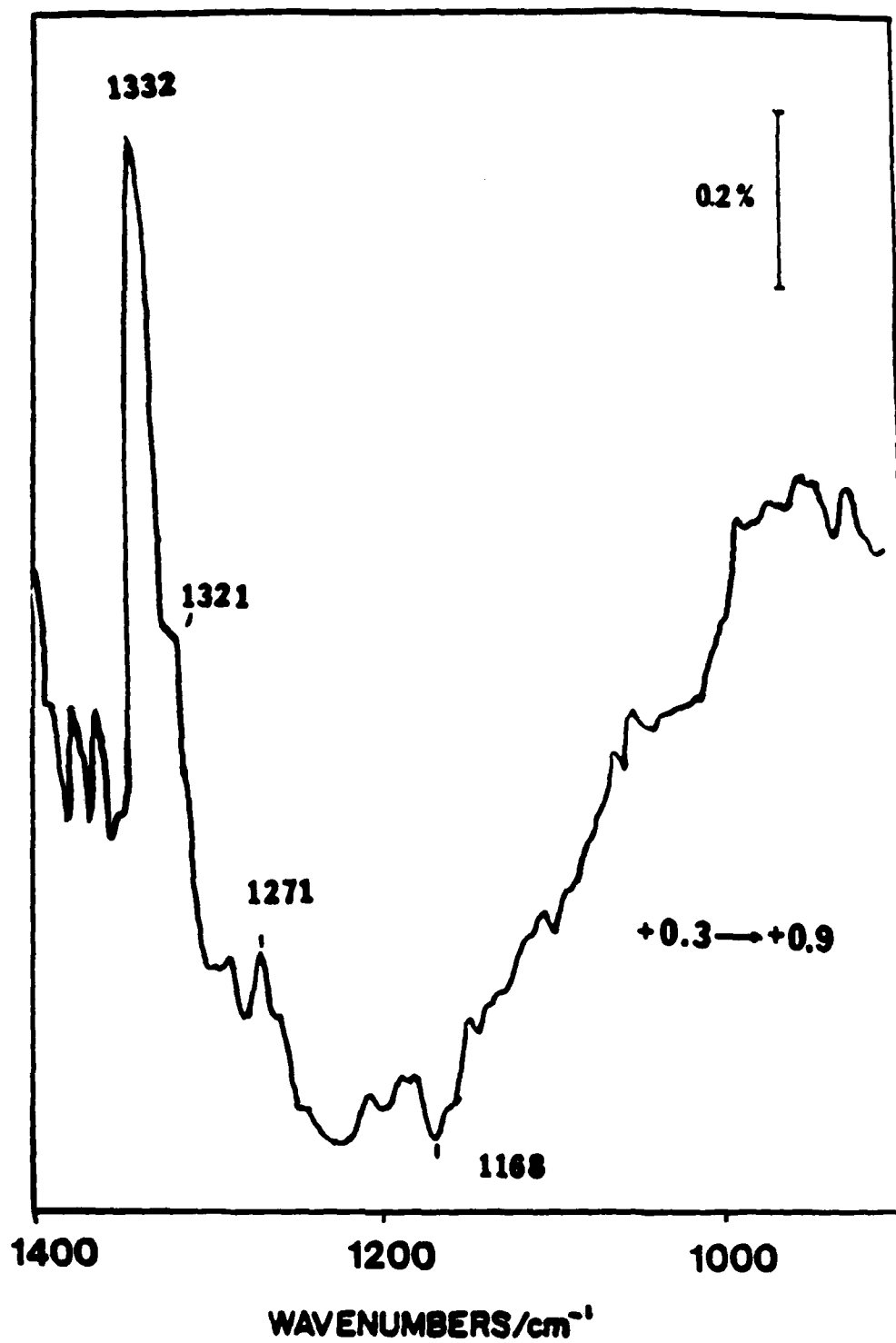
Figure 5. SNIFTIRS spectra at (a) -1.0 V and (b) -1.5 V (SCE) following a potential step to anodic potentials (+0.9 V). The base potential is +0.3 V. The solution contains SO_2 in 1.0 M H_2SO_4 .

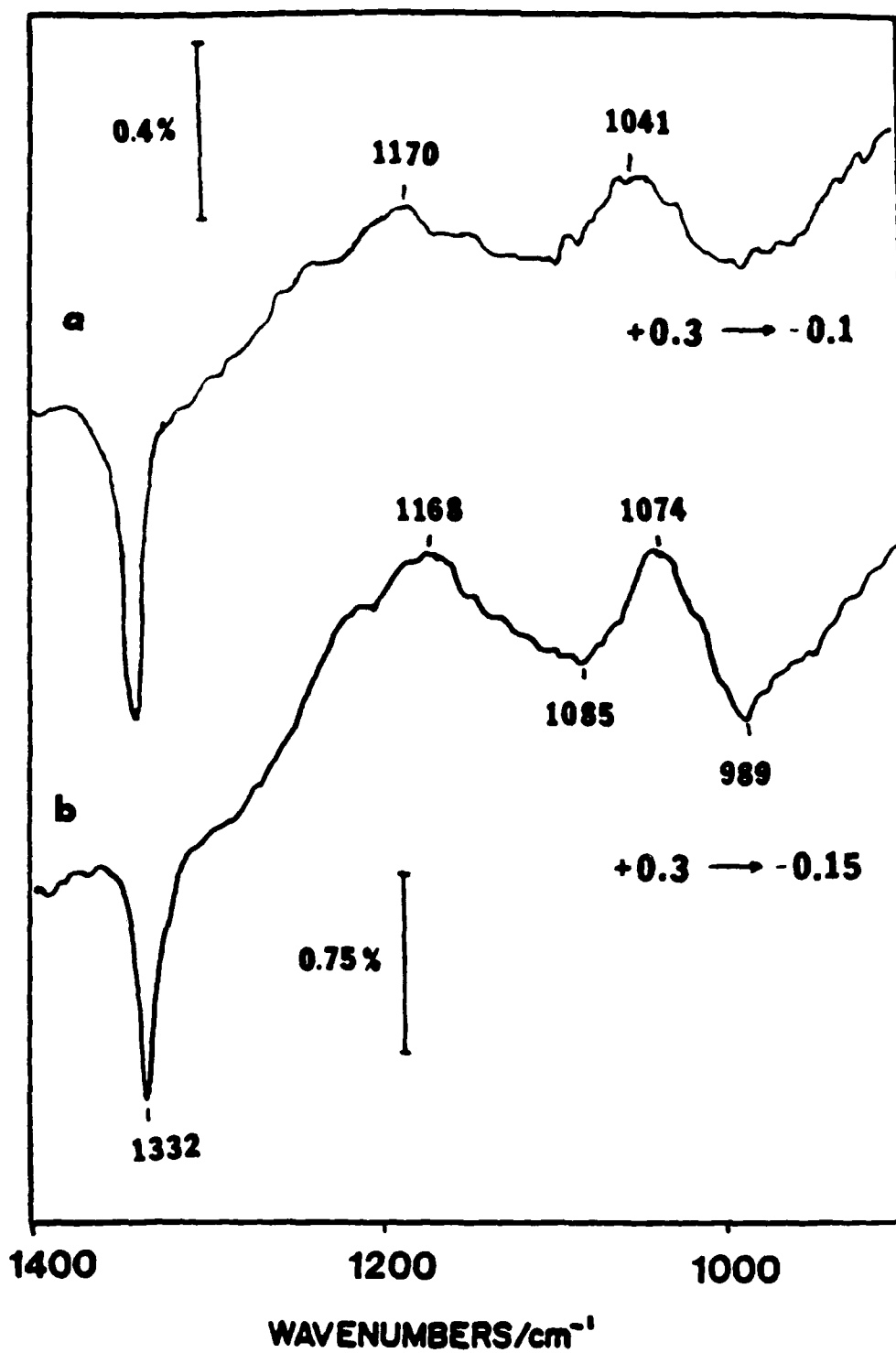
Figure 6. Same as Figure 5 showing a higher energy spectral region.

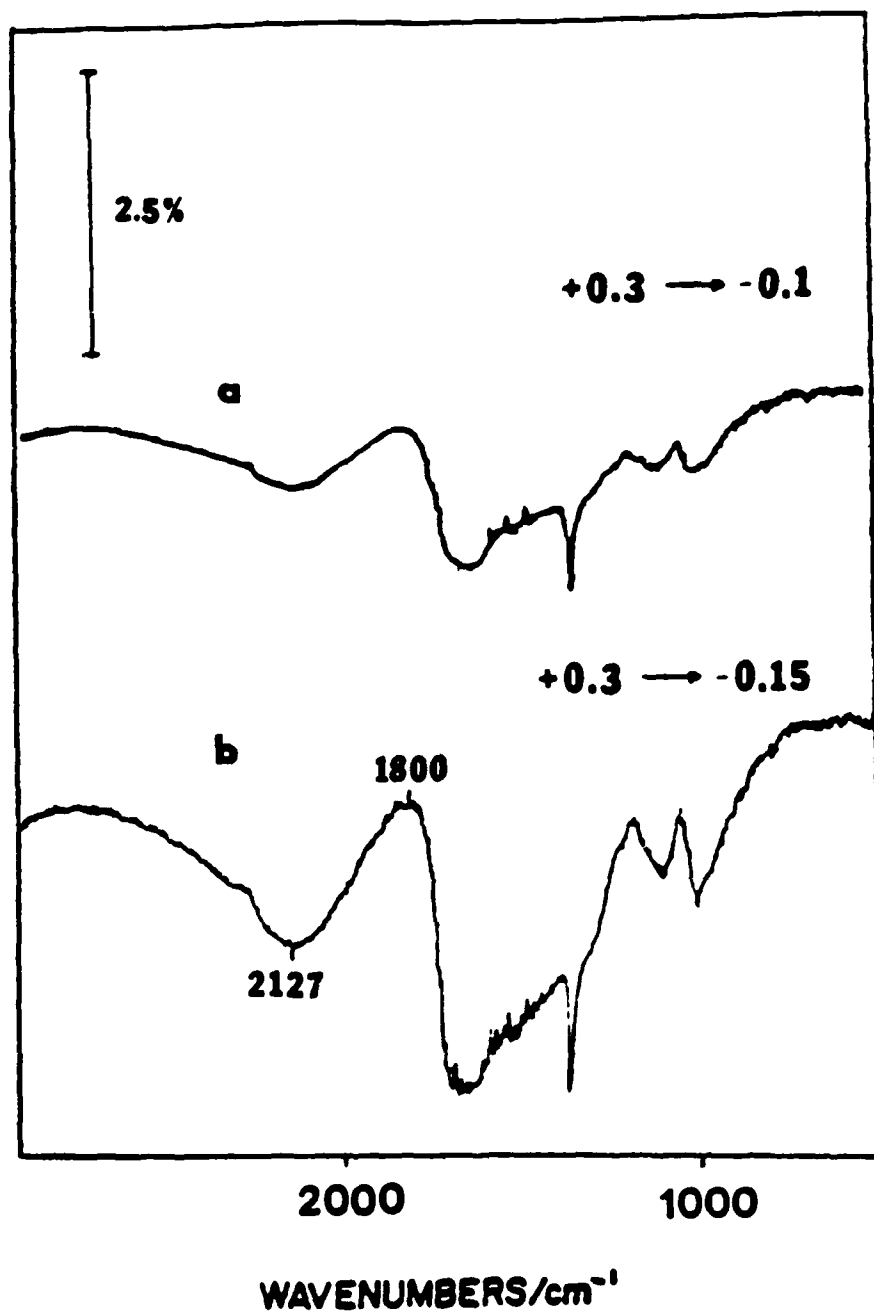












TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

ABSTRACTS DISTRIBUTION LIST, SDIO/IST

Dr. Robert A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Douglas N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, UT 84602

Dr. Stanley Pons
~~Department of Chemistry~~
~~University of Utah~~
Salt Lake City, UT 84112

Dr. H. V. Venkatesetty
Honeywell, Inc.
10701 Lyndale Avenue South
Bloomington, MN 55420

Dr. J. Foos
EIC Labs Inc.
111 Downey St.
Norwood, MA 02062

Dr. Neill Weber
Ceramtec, Inc.
163 West 1700 South
Salt Lake City, UT 84115

Dr. Subhash C. Narang
SRI International
333 Ravenswood Ave.
Menlo Park, CA 94025

Dr. J. Paul Pemsler
Castle Technology Corporation
52 Dragon Ct.
Woburn, MA 01801

Dr. R. David Rauh
EIC Laboratory Inc.
111 Downey Street
Norwood, MA 02062

Dr. Joseph S. Foos
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Donald M. Schleich
Department of Chemistry
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 01

Dr. Stan Szpak
Code 633
Naval Ocean Systems Center
San Diego, CA 92152-5000

Dr. George Blomgren
Battery Products Division
Union Carbide Corporation
25225 Detroit Rd.
Westlake, OH 44145

Dr. Ernest Yeager
Case Center for Electrochemical
Science
Case Western Reserve University
Cleveland, OH 44106

Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, CA 93555

Dr. Ashok V. Joshi
Ceramtec, Inc.
2425 South 900 West
Salt Lake City, Utah 84119

Dr. W. Anderson
Department of Electrical &
Computer Engineering
SUNY - Buffalo
Amherst, Massachusetts 14260

Dr. M. L. Gopikanth
Chemtech Systems, Inc.
P.O. Box 1067
Burlington, MA 01803

Dr. H. F. Gibbard
Power Conversion, Inc.
495 Boulevard
Elmwood Park, New Jersey 07407

ABSTRACTS DISTRIBUTION LIST, SDIO/IST

Dr. V. R. Koch
Covalent Associates
52 Dragon Court
Woburn, MA 01801

Dr. Randall B. Olsen
Chronos Research Laboratories, Inc.
4186 Sorrento Valley Blvd.
Suite H
San Diego, CA 92121

Dr. Alan Hooper
Applied Electrochemistry Centre
Harwell Laboratory
Oxfordshire, OX11 0RA UK

Dr. John S. Wilkes
Department of the Air Force
The Frank J. Seiler Research Lab.
United States Air Force Academy
Colorado Springs, CO 80840-6528

Dr. Gary Bullard
Pinnacle Research Institute, Inc.
10432 N. Tantan Avenue
Cupertino, CA 95014

Dr. J. O'M. Bockris
Ementech, Inc.
Route 5, Box 946
College Station, TX 77840

Dr. Michael Binder
Electrochemical Research Branch
Power Sources Division
U.S. Army Laboratory Command
Fort Monmouth, New Jersey 07703-5000

Professor Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton, Hants, SO9 5NH UK